First Order Static Excitation Potential: Scheme for Excitation Energies and Transition Moments

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We present an approximation scheme for the calculation of the principal excitation energies and transition moments of finite many-body systems. The scheme is derived from a first order approximation to the self energy of a recently proposed extended particle-hole Green's function. A hermitian eigenvalue problem is encountered of the same size as the well-known random phase approximation (RPA). We find that it yields a size consistent description of the excitation properties and removes an inconsistent treatment of the ground state correlation by the RPA. By presenting a hermitian eigenvalue problem the new scheme avoids the instabilities of the RPA and should be well suited for large scale numerical calculations. These and additional properties of the new approximation scheme are illuminated by a very simple exactly solvable model.

INTRODUCTION

Many–body Green's function theory has provided several standard approximation schemes for the calculation of excitation properties in atoms, molecules, and atomic nuclei. Setting out from a convenient single–particle description like the Hartree–Fock approximation, these schemes usually lead to a matrix eigenvalue problem. This supplies approximations for the excitation energies and transition operator matrix elements of the system. The starting point is usually the well–known *polarisation propagator* [1], a fundamental two–particle Green's function of nonrelativistic many–body theory. It is given by a sum of two terms that are related by symmetry (see e. g. Ref. [2]).

$$\Pi_{rs,r's'}(\omega) = \Pi^{ph}_{rs,r's'}(\omega) + \Pi^{hp}_{rs,r's'}(\omega) \tag{1}$$

The so–called *particle–hole part* $\Pi^{ph}_{rs,r's'}(\omega)$ already contains all the physically relevant information exhibiting single poles in the energy variable ω at the exact excitation energies of the system. Its name originates in the single particle picture which is usually taken as the zeroth order in a perturbation theoretical treatment. Zeroth order contributions to Π^{ph} only arise if the indices r and r' are particle indices and s and s' hole indices. We speak of a particle index if it refers to a virtual single–particle state, i. e. a state which is not occupied in a Slater determinant ground state whereas a hole index refers to an occupied single–particle state. The particle–hole part thus primarily describes excitations which, in a single–particle picture, may be understood as lifting one fermion from an occupied orbital to a virtual one. In a correlated system, however, there are no fully occupied or fully virtual single–particle states and thus the exact particle–hole part contributes also for index pairs (r, s) other than particle–hole index pairs.

The various approximation schemes may be classified by the order in which the correlation is taken into account. Another criterion for classification is which parts of the polarisation propagator are included.

A simple first order approximation scheme based on Π^{ph} is the so–called *Tamm–Dancoff Approximation (TDA)* [1,3]. It can be seen as the first order approximation to the inverse matrix of the particle–hole part. In a quantum chemical language the TDA may be understood as treating the excited states on the single–excitation Configuration Interaction (SCI) level in comparison to an uncorrelated ground state. The *Algebraic Diagrammatic Construction (ADC)* approach [2,4] represents a family of systematic higher order approximation schemes to the particle–hole part.

Another group of approximations results from including the second part of the polarisation propagator $\Pi^{hp}_{rs,r's'}(\omega)$. This part is called *hole–particle part* because its zeroth order vanishes unless r and r' are hole indices and s and s' are particle indices. In contrast to the particle–hole part its poles appear at the negative excitation energies. The fundamental first order approximation scheme which treats both parts of the polarisation propagator on an equal footing is the so–called *Random Phase Approximation (RPA)* [5,6,1,3]. Among the many different ways of deriving this approximation we want to focus on the role of the RPA as the first order approximation to the inverse matrix of the polarisation propagator (1). Naturally this matrix now comprises the set of particle–hole as well as hole–particle configurations and therefore has twice the dimension of the TDA matrix. Among the higher order schemes that treat both parts of the polarisation propagator we want to mention the *Second Order Polarisation Propagator Approximation (SOPPA)* [7,8,9] and the *Equation of Motion (EOM)* method [6,10].

In the Configuration Interaction picture the RPA may be seen to include ground state correlation in addition to the correlation of the excited states already accounted for in the TDA [8,11]. The RPA does so, however, in a non–variational manner and thus it is not obvious that the RPA yields improved results compared to the TDA. It has rather been observed that in certain cases the RPA excitation energies are worse than those of the TDA, also in systems where correlation of the ground state is of special importance (for exemplary numerical comparisons see e. g. [12,13]). In fact we will see later that the influence of ground state correlation onto the RPA excitation energies has to be regarded inconsistent with Rayleigh–Schrödinger perturbation theory (see also Ref. [2]). We will further study a simple model system for which the RPA gives much poorer results than the TDA. For this example a new approximation method, called *First Order Static Excitation Potential (FOSEP)*, yields the exact solution while posing a matrix eigenvalue problem of the same size as the RPA. Also a perturbation theoretical analysis shows that FOSEP consistently includes ground state correlation.

The FOSEP method is a first order approximation scheme that is derived from an *extended particle–hole Green's function* [14] where additionally to the particle–hole and the hole–particle parts other propagator terms are present: The polarisation propagator has been augmented by combinations of single–particle propagators that give rise to additional zeroth order contributions in the particle–particle and the hole–hole index space. The introduced terms are chosen such that the extended Green's function now satisfies a *Dyson equation* which in turn defines a well–behaved *(particle–hole) self energy* in analogy to the fundamental single–particle Green's function [1,15,16]. Earlier we have applied the general procedure to the particle–particle propagator, another well–known two–particle Green's function. We could show that the self–energy of a suitably chosen extended two–particle Green's function serves as an optical potential for elastic scattering of two–particle projectiles [17]. The particle–hole self energy, in turn, may be understood as a sort of "optical potential for particle–hole excitations", some general aspects of which are discussed in Ref. [14].

This paper is organised as follows: After a brief review of the relevant construction principles of the extended particle–hole Green's functions we will define the FOSEP approximation and discuss the structure of the corresponding matrix eigenvalue problem in Sec. I. In the next section the properties of the FOSEP approximation for excitation energies and transition moments are investigated on a formal level. First the similarity to the RPA equations is pointed out in order to compare the properties of the two approximations (II A). Both schemes share the fundamental properties of size consistency (II B) and the invariance under unitary transformations of the occupied or virtual Hartree–Fock orbitals (II C). The differences between the two approximations will become apparent in Sec. II D when we will perform a perturbation theoretical analysis of the excitation energies up to second order. This analysis shows that the FOSEP approximation includes part of the ground state correlation in a consistent way while the RPA proves inconsistent with perturbation theory in this respect. It follows an analysis of the approximation for transition moments which is found to be consistent in first order. The last paragraph of Sec. II deals with the equivalence of length and velocity form of the transition moments of the dipole operator which are important for the so–called oscillator strengths. In Sec. III the FOSEP method is compared with the RPA and TDA in application to a simple exactly solvable model system.

I. THE FOSEP APPROXIMATION

The extended particle–hole Green's function is one species in a family of two–particle propagators that fulfil Dyson's equation. The general theory has been developed in Ref. [14,17]. Here we will only outline the main ideas that are relevant in the present context. The desired physical information like excitation energies and transition moments is contained in the poles and residues of the extended Green's function. Calculating these is equivalent to solving the eigenvalue problem related to a generalised excitation energy operator $\hat{\mathcal{H}}$ which lives in an extended Hilbert space Y. Throughout this paper we assume a discrete eigenvalue spectrum for the relevant Hamiltonians since we are interested in finite basis set approximations. The generalisation to continuous spectra, however, poses no particular problem.

A basis of the extended Hilbert space Y is given by the set of states $\{\,|Q_I\rangle\,\}$ which are chosen "orthonormal" with respect to an indefinite metric $\hat{\mu}$:

$$\langle Q_I|\,\hat{\mu}\,|Q_J\rangle = \pm\delta_{IJ} \tag{2}$$

A model space is spanned within the full space by a subset of basis states $\{|Y_{rs}\rangle\}$. This model space is supposed to allow the description of those excitations that are predominantly of particle–hole type. Direct reference to 'occupied' and 'virtual' single–particle states is avoided by allowing the indices r and s to range over the full set of single–particle indices each. The states $|Y_{rs}\rangle$ are chosen to include (ground state) correlation being 'correlated excited states' in the sense of Refs. [18,19]. On the other hand they are constructed manifestly 'orthonormal', i. e. satisfying

$$\langle Y_{rs}|\hat{\mu}|Y_{r's'}\rangle = \delta_{rr'}\delta_{ss'} \tag{3}$$

exactly and in each order of perturbation theory. It is a special property that all states in the primary subset $\{|Y_{rs}\rangle\}$ have positive norm. The construction of states with the described properties presents the crucial step in developing the theory of extended particle–hole Green's functions. Explicit expressions for the particular choice used in this paper can be found in Ref. [14] together with a thorough discussion of the construction principles and the remaining freedom of choice.

The basis $\{\,|Q_I\rangle\}$ defines a matrix representation $\underline{\underline{\mathcal{H}}}$ of the generalised excitation energy operator $\hat{\mathcal{H}}$. The subdivision of the basis into the basis of the model space $\{|Y_{rs}\rangle\}$ and the complementary part superposes a block structure onto this matrix:

$$\underline{\underline{\mathcal{H}}} = \left(\begin{array}{cc} \underline{\underline{\mathcal{H}}}_{aa} & \underline{\underline{\mathcal{H}}}_{ab} \\ \underline{\underline{\mathcal{H}}}_{ba} & \underline{\underline{\mathcal{H}}}_{bb} \end{array} \right) \tag{4}$$

The index a refers to the model space and b to its complement. The primary block $\underline{\underline{\mathcal{H}}}_{aa}$ of this matrix is given by

$$\left[\underline{\underline{\mathcal{H}}}_{aa} \right]_{rs,r's'} = \langle Y_{rs}|\hat{\mu}\hat{\mathcal{H}}|Y_{r's'}\rangle. \tag{5}$$

Explicit expressions for this matrix may be found in the appendix and are derived in Ref. [14] where also a physical interpretation as a static particle–hole scattering potential in the case of Coulomb interacting particles is given. In the following we will investigate the first order approximation to this matrix within the framework of many–body perturbation theory.

In order to apply perturbation theory the many–body Hamiltonian $\hat{H}$ has to be split into two parts $\hat{H}_o$ and $\hat{H}_1$ as usual. The choice of the one–particle operator

$$\hat{H}_o = \sum_i \varepsilon_i \, a_i^\dagger a_i \tag{6}$$

as characterised by the diagonalising single–particle basis $\{\,|\varphi_i\rangle\}$ and single–particle energies $\{\varepsilon_i\}$ defines the zeroth order of perturbation theory. The residual interaction $\hat{H}_1 = \hat{v} + \hat{V}$ contains contributions of a one–particle operator $\hat{v}$ and a two–body interaction $\hat{V}$:

$$\hat{v} = \sum_{i,j} v_{ij} \, a_i^\dagger a_j \tag{7}$$

$$\hat{V} = \frac{1}{2} \sum_{i,j,k,l} V_{ijkl} \, a_i^\dagger a_j^\dagger a_l a_k \tag{8}$$

In particular we are interested in the Møller–Plesset partitioning of the Hamiltonian where the zeroth order Hamiltonian $\hat{H}_o$ is defined by the Hartree–Fock approximation. In the case of a nondegenerate ground state the matrix elements v_{ij} of the one–particle part of the interaction are then given by

$$v_{ij}^{HF} = -\sum_k n_k V_{ik[jk]}. \tag{9}$$

Here $V_{rs[r's']} = V_{rsr's'} - V_{rss'r'}$ denotes the anti–symmetrised matrix element of the two–body interaction and n_r is the occupation number of the orbital $|\varphi_r\rangle$ in the zeroth order ground state Slater determinant $|\Phi_o\rangle$.

The zeroth order of the primary block $\underline{\underline{\mathcal{H}}}_{aa}$ from Eq. (5) yields the matrix $\underline{\varepsilon}$ of zeroth order excitation energies:

$$\left[\underline{\underline{\mathcal{H}}}_{aa} \right]^{(0)}_{rs,r's'} = \left[\underline{\varepsilon} \right]_{rs,r's'} = (\varepsilon_r - \varepsilon_s)\, \delta_{rr'}\delta_{ss'} \tag{10}$$

This reflects the fact that in our ansatz the first index in the pair rs has to be understood as marking the orbital (position) into which a particle is created and the second index as marking the orbital where a particle is destroyed (or a hole created).

The main motivation for developing the theory of the extended particle–hole Green's function was that it fulfils a Dyson equation and therefore possesses a particle–hole self energy $\underline{\underline{\mathcal{S}}}(\omega)$ [14,17]. This self energy may be seen to result from a partitioning of the eigenvalue problem associated to the matrix $\underline{\underline{\mathcal{H}}}$ with respect to the primary block $\underline{\underline{\mathcal{H}}}_{aa}$. The energy independent ("static") part of the self energy $\underline{\underline{\mathcal{S}}}(\infty)$ is defined by the primary block minus its zeroth order:

$$\underline{\underline{\mathcal{S}}}(\infty) = \underline{\underline{\mathcal{H}}}_{aa} - \underline{\varepsilon} \tag{11}$$

The significance of this part is to describe the the influence of correlation to particle–hole excitations that remains in the high energy limit, i. e. when the "target particles have no time to rearrange upon the influence of the particle–hole excitation". The lowest order contributions to this matrix are of first order. The energy dependent ("dynamic") part of the self energy $\underline{\underline{\mathcal{S}}}(\omega) - \underline{\underline{\mathcal{S}}}(\infty)$ takes account of the remaining blocks of the matrix $\underline{\underline{\mathcal{H}}}$ and starts in second order.

The first order contributions to the (static) self energy are given by

$$\left[\underline{\underline{\mathcal{S}}}(\infty)\right]^{(1)}_{rs,r's'} = \left[\underline{\underline{\mathcal{H}}}_{aa}\right]^{(1)}_{rs,r's'} = v_{rr'}\delta_{ss'} - v_{s's}\delta_{rr'}$$
$$+ V_{rs'[sr']}\left(\overline{n}_r n_s - n_r \overline{n}_s\right)\left(\overline{n}_{r'} n_{s'} - n_{r'} \overline{n}_{s'}\right)$$
$$+ \delta_{ss'}\sum_k n_k V_{rk[r'k]} - \delta_{rr'}\sum_k n_k V_{s'k[sk]} \tag{12}$$

for a general Hamiltonian where we have introduced the notation $\overline{n}_r = 1 - n_r$. Expression (12) may be readily derived from the general expression for the primary block $\underline{\underline{\mathcal{H}}}_{aa}$ which can be found in the appendix. In the Møller–Plesset case (9), the first order simplifies even further. In particular it is this approximation that we will refer to as *First Order Static Excitation Potential (FOSEP)*:

$$\left[\underline{\underline{\mathcal{S}}}^{FOSEP}\right]_{rs,r's'} = V_{rs'[sr']}\left(\overline{n}_r n_s - n_r \overline{n}_s\right)\left(\overline{n}_{r'} n_{s'} - n_{r'} \overline{n}_{s'}\right) \tag{13}$$

Now the following hermitian eigenvalue problem remains to be solved:

$$\left(\underline{\underline{\varepsilon}} + \underline{\underline{\mathcal{S}}}^{FOSEP}\right)\underline{X} = \omega\underline{X} \tag{14}$$

The (physical) eigenvalues ω provide approximations to the excitation energies of the system and the corresponding eigenvectors $\underline{X}$ may be used to calculate transition operator matrix elements (transition moments). The transition moments corresponding to the dipole operator define the so–called oscillator strengths which are of great importance for photo–absorption and emission processes [8]. The FOSEP approximation for transition operator matrix elements reads [14]

$$\langle\Psi_o|\hat{T}|\Psi_\mu\rangle^{FOSEP} = \sum_{ij} T^{ij} X^\mu_{ij}, \tag{15}$$

where T^{ij} are the matrix elements of the (one–particle) transition operator $\hat{T}$ and X^μ_{ij} are the components of the eigenvector associated to an excitation into the state $|\Psi_\mu\rangle$.

Due to extensions included in the definition of the primary states $|Y_{rs}\rangle$, however, not all of the eigenvalues and eigenvectors of Eq. (14) correspond to "physical" excitations. More insight may be gained by looking at the particular block structure of this eigenvalue problem which is revealed when splitting the set of index pairs according to whether the indices relate to occupied (hole) or unoccupied (virtual or particle) orbitals. In zeroth order only the diagonal matrix $\underline{\underline{\varepsilon}}$ is present and the distinction between "physical" and "unphysical" excitations is obvious, since the ground state is approximated by a Slater determinant. In this case excitations of a single particle are possible only from an occupied into a virtual orbital. Thus only the *ph–ph* block is "physical". In the first order (FOSEP) approximation the secular matrix has the following structure:

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$$\underline{\underline{\varepsilon}} + \underline{\underline{S}}^{FOSEP} =
\begin{array}{c|c|c|c|c|}
 & hh & ph & hp & pp \\
\hline
hh & \underline{\underline{\varepsilon}}^{hh} & 0 & 0 & 0 \\
\hline
ph & 0 & \underline{\underline{\varepsilon}}^{ph} + \underline{\underline{V}} & \underline{\underline{W}} & 0 \\
\hline
hp & 0 & \underline{\underline{\tilde{W}}}^{*} & -\underline{\underline{\tilde{\varepsilon}}}^{ph} + \underline{\underline{\tilde{V}}}^{*} & 0 \\
\hline
pp & 0 & 0 & 0 & \underline{\underline{\varepsilon}}^{pp} \\
\hline
\end{array}
\tag{16}$$

The asterisk (*) denotes complex conjugation for the matrix elements and the tilde ($\tilde{}$) denotes a simultaneous transposition of the two index pairs that specify a matrix element which simply means a renumbering of the rows and columns of that matrix:

$$\left[\underline{\underline{\tilde{A}}}\right]_{rs,r's'} = \left[\underline{\underline{A}}\right]_{sr,s'r'}$$

First of all we notice that the FOSEP self energy $\underline{\underline{S}}^{FOSEP}$ does not contribute at all for pairs of orbitals that are both occupied (hh) or both virtual (pp) and only the zeroth order matrix $\underline{\underline{\varepsilon}}$ remains. Thus the hh–hh and pp–pp blocks decouple from the rest of the matrix and the eigenvalue problem (14) for these blocks becomes trivial, simply yielding the Hartree–Fock orbital energy differences. These blocks are obviously not correlated in the first order treatment. We want to mention that this decoupling of the hh–hh and pp–pp blocks is special to the Møller–Plesset partitioning of the Hamiltonian and to the particular choice of the extended states $|Y_{rs}\rangle$ considered in this paper. It does not appear for other choices discussed in Ref. [14]. The decoupling leads to a considerable reduction of numerical effort and therefore justifies the present choice. Many of the properties discussed in the present paper, however, generalise also to first order approximations based upon other choices for the primary extended states $|Y_{rs}\rangle$.

The ph block of the $\underline{\underline{\varepsilon}}$ matrix $\underline{\underline{\varepsilon}}^{ph}$ contains those energies that relate to a simple particle–hole excitation in a zeroth order picture. The contribution of

$$\left[\underline{\underline{V}}\right]_{ph,p'h'} = V_{ph'[hp']} \qquad (h,\, h' \text{ occupied},\, p,\, p' \text{ virtual orbitals}) \tag{17}$$

in the ph–ph block describes the interaction of the uncorrelated ground state Slater determinant with a singly excited configuration. In fact, diagonalising the ph–ph block $\underline{\underline{\varepsilon}}^{ph} + \underline{\underline{V}}$ on its own results in the well–known *Tamm–Dancoff Approximation (TDA)* [1]. The coupling $\underline{\underline{W}}$ to the hp–hp block can be understood as taking into account ground state correlation as will be explained later with the help of perturbation theoretical arguments. A similar coupling also appears in the *Random Phase Approximation (RPA)* [1]. The relation of our approach to the RPA will be discussed in detail below.

The hp–hp block by itself does not seem very physical in character at all. Its zeroth order excitation energies are negative and result from creating a hole in a virtual orbital and a particle in an occupied orbital. Nevertheless, the hp–hp block couples through the matrix

$$\left[\underline{\underline{W}}\right]_{ph,h'p'} = -V_{pp'[hh']} \qquad (h,\, h' \text{ occupied},\, p,\, p' \text{ virtual orbitals}) \tag{18}$$

with the physical ph–ph block and thus introduces a correction to the Tamm–Dancoff excitation energies. Due to the decoupling of the pp and hh blocks we are left with an eigenvalue problem comprising the blocks of the FOSEP matrix with ph and hp indices:

$$\underline{\underline{M}}^{FOSEP}\, \underline{x} = \omega\, \underline{x} \tag{19}$$

$$\underline{\underline{M}}^{FOSEP} = \underline{\underline{\varepsilon}} + \underline{\underline{S}}^{FOSEP}\Big|_{ph \text{ and } hp \text{ blocks}} = \begin{pmatrix} \underline{\underline{\varepsilon}}^{ph} + \underline{\underline{V}} & \underline{\underline{W}} \\ \underline{\underline{\tilde{W}}}^{*} & -\underline{\underline{\tilde{\varepsilon}}}^{ph} + \underline{\underline{\tilde{V}}}^{*} \end{pmatrix} \tag{20}$$

This is the eigenvalue problem that has to be solved in the FOSEP approximation scheme. In contrast to the RPA it is a hermitian eigenvalue problem always yielding real eigenvalues. In fact, in most cases the matrix $\underline{\underline{M}}^{FOSEP}$ is real symmetric.

As long as the interaction remains weak enough, there is a clear distinction between "physical" eigenvalues of this matrix and "unphysical" ones by the sign of these energies. Even with stronger interaction the distinction may still be valid. This is understood easily when considering a model system where the ph–ph block has the dimension one and all matrix elements are real. The matrix $\underline{\underline{M}}^{FOSEP}$ then is two by two and its eigenvalues are given by

$$\pm\sqrt{\varepsilon^{ph\,2} + W^2} + V.$$

Thus we get one positive eigenvalue and a negative one, provided that

$$V^2 < \varepsilon^{ph\,2} + W^2.$$

Note that V is the contribution of the correlation introduced in the TDA and this condition now states that it has to be small enough compared to the zeroth order excitation energy augmented by the additional interaction term W. When this condition is violated, or in general the numbers of positive and negative eigenvalues in a given symmetry are not the same, the eigenvectors may be necessary to distinguish between physical and unphysical contributions. Still the "physical" approximation may usually be defined by the upper half of the eigenvalues.

In the remaining sections of this paper we will discuss the FOSEP approximation as defined above. It presents the natural first step in approximating the particle–hole self energy $\underline{\underline{S}}(\omega)$ and thus the matrix $\underline{\underline{H}}$. At this place we want to mention that other approximations, for example, result by augmenting the primary set of states $|Y_{rs}\rangle$. In particular one can obtain the RPA straightforwardly via the formalism of extended Green's functions. This is achieved by additionally including a subset of the basis $\{\,|Q_I\rangle\}$ consisting of states with negative norm that are degenerate (in zeroth order) to the hole–particle fraction of the set $\{|Y_{rs}\rangle\}$ [14]. This augmented set of states defines an extension of the primary block $\underline{\underline{H}}_{aa}$ in the matrix $\underline{\underline{H}}$. In first order this extended matrix can be decoupled with the help of a unitary transformation into the RPA eigenvalue problem and additional unphysical blocks. Thus the RPA is included in the general theory as a specific approximation. Note, however, that FOSEP presents the *canonical* first order approximation in our ansatz since it is based upon the primary set of states $\{|Y_{rs}\rangle\}$ which defines the Green's function and self energy matrices.

II. PROPERTIES OF THE FOSEP APPROXIMATION

In this chapter we will discuss some general properties of the FOSEP approximation. In order to elucidate the relation to the well known first order approximation schemes RPA and TDA we start with briefly reformulating the RPA in our notation. We go on with considering two fundamental invariances FOSEP shares with RPA and TDA namely size consistency and invariance with respect to unitary transformations of the single–particle basis. In order to show the differences between the three schemes we will carry out a perturbation theoretical analysis for the excitation energies as well as for the transition moments. Finally, the equivalence of length and velocity form of the dipole operator transition moments is discussed.

A. Relation to the RPA

The *Random Phase Approximation (RPA)* [1,3] for the calculation of excitation energies and transition operator matrix elements in finite Fermi systems may be derived and understood in many different ways. Traditionally the RPA is derived by the infinite summation of a certain type of diagrams in the Feynman–Dyson perturbation series of the polarisation propagator [5]. Equivalently it can be understood as a first order approximation to the integral kernel of the Bethe–Salpeter equation [20] or as a specific first order approximation in the equation of motion of the polarisation propagator [6,8]. Now we are going to present the RPA equations in a form suitable for comparison with FOSEP.

Based upon a Hartree–Fock zeroth order the RPA is defined by the following eigenvalue problem [21]:

$$\left(\underline{\underline{\varepsilon}}\,\underline{m} + \underline{R}\right)\underline{x} = \omega\,\underline{m}\,\underline{x} \tag{21}$$

The matrix $\underline{\underline{\varepsilon}}$ is defined like above in Eq. (10). The RPA kernel $\underline{R}$ consists of the matrix elements $R_{rs,r's'} = V_{rs'[sr']}$ and the metrical matrix $\underline{m}$ by

$$\left[\underline{\underline{m}}\right]_{rs,r's'} = \delta_{rr'}\delta_{ss'}\left(\overline{n}_r n_s - n_r \overline{n}_s\right). \tag{22}$$

Note that in block matrix notation $\underline{\underline{m}}$ can be written as

$$\underline{\underline{m}} = \begin{pmatrix} \underline{\underline{1}} & \underline{\underline{0}} \\ \underline{\underline{0}} & -\underline{\underline{1}} \end{pmatrix}. \tag{23}$$

All these matrices are indexed by pairs of single–particle indices that are required to be either particle–hole or hole–particle index pairs. Thus the RPA eigenvalue problem has the same size as the FOSEP one (19). The essential difference is the appearance of the indefinite metric $\underline{\underline{m}}$ in the RPA case which renders the RPA problem a non–hermitian eigenvalue problem. As a consequence the RPA may become instable and lead to complex eigenvalues [8]. The RPA kernel $\underline{\underline{R}}$ is related to the FOSEP self energy $\underline{\underline{S}}^{FOSEP}$ in the following way:

$$\underline{\underline{S}}^{FOSEP} = \underline{\underline{m}}\,\underline{\underline{R}}\,\underline{\underline{m}} \tag{24}$$

Introducing the matrix

$$\underline{\underline{M}}^{RPA} = \underline{\underline{\varepsilon}}\,\underline{\underline{m}} + \underline{\underline{S}}^{FOSEP}\Bigg|_{ph \text{ and } hp \text{ blocks}} = \begin{pmatrix} \underline{\underline{\varepsilon}}^{ph} + \underline{\underline{V}} & \underline{\underline{W}} \\ \underline{\underline{\tilde{W}}}^* & \underline{\underline{\tilde{\varepsilon}}}^{ph} + \underline{\underline{\tilde{V}}}^* \end{pmatrix} \tag{25}$$

with the same nomenclature as in (17) and (18), the RPA eigenvalue problem may be rewritten to

$$\underline{\underline{M}}^{RPA}\,\underline{x}' = \omega\,\underline{\underline{m}}\,\underline{x}' \tag{26}$$

with $\underline{x}' = \underline{\underline{m}}\,\underline{x}$. Comparing the RPA (26, 25) with the FOSEP eigenvalue problem (19, 20) we see that both have the same size and start from the same input data while the difference lies in some minus signs. Before analysing the differences further we want to discuss two fundamental properties that are shared by both schemes.

B. Size Consistency of FOSEP

The question of size consistency of a many–body method is the question of whether the resulting approximations for physical quantities scale correctly with the size of the system [22,23]. The general question is difficult to answer and usually one has to resort to simple models or numerical calculations. Nevertheless, this concept becomes very important for applications to large or extended systems. In the context of finite systems, especially molecules, the so–called separate fragment model provides a useful test of correct scaling behaviour. We consider a many–body system consisting of two or more separate (noninteracting) subsystems (fragments). Size consistency of excitation energies and transition moments then means that an excitation that is local to one of the subsystems is approximated with the same result regardless whether the approximation scheme is applied to the full system or only to the fragment. A sufficient but not necessary condition for this property is that the secular equations of the approximation scheme give rise to independent sets of equations corresponding to local excitations on the individual subsystems. This 'a priori' decoupling of independent, local equations is known as the separability property [24].

The separability of FOSEP and RPA is proven by the following arguments: In the model of separating fragments the Hamiltonian of the full system is given by the sum of the Hamiltonians of the subsystems. This implies that the (Hartree–Fock) single–particle states φ_r may be chosen local to either fragment and that the matrix elements of the two–body interaction V_{ijkl} vanish unless all indices $ijkl$ relate to states belonging to the same subsystem. From the definition of the FOSEP matrix (13, 20) and the RPA matrix (25) it therefore becomes clear that both methods have the separability property and thus can be regarded size consistent. The same arguments apply to the TDA to which the FOSEP and RPA reduce in the case of vanishing coupling $\underline{\underline{W}}$ as explained in Sec. I. For nonlocal excitations the excitation energy is simply given by the difference of the single–particle (Hartree–Fock) energies for all three schemes. This means that the level of approximation is that of Koopman's theorem which provides a consistent first order description. We want to mention that the separability property is by no means a matter of course for more accurate many–body methods like, for example, the general CI method [25].

C. Unitary Transformations of Single–Particle Orbitals

In order to separate the influence of finite truncations of the underlying single–particle basis from the systematic deficiencies of a given approximation scheme it is important that the approximation is invariant with respect to

rotations of the single–particle basis. A global invariance is self–evident only for 'exact' methods like full CI. Systematic truncations of the CI matrix employing single, double, or triple excitations on a given reference configuration are at least invariant with respect to transformations of the single particle basis that do not mix occupied and virtual orbitals. Such an invariance usually does not apply for perturbative propagator methods. The FOSEP method as well as the RPA and the TDA, however, share this invariance with the CI whereas higher order methods usually do not. For the SOPPA method the influences of rotations of the orbital set have been investigated numerically [26].

A physical motivation for altering the single–particle functions may be drawn from the fact that the Hartree–Fock virtual orbitals describe additional test particles in a mean field and therefore constitute rather diffuse functions while the main effects of correlation show up at short range due to ineffective screening. Thus one can hope to achieve a better description of the influence of correlation with more localised virtual orbitals than the Hartree–Fock ones.

Within a perturbation theoretical approach a unitary transformation within the set of virtual single–particle states can be realised by adding a (hermitian) single–particle potential to $\hat{H}_o$ of Eq. (6) that takes effect only on the virtual orbitals and subtracting it again from $\hat{H}_1$ of Eq. (7). The new single–particle basis is then defined as the diagonalising basis for the new zeroth order Hamiltonian. Obviously the new basis is connected to the original one by a unitary transformation that leaves invariant the occupied single–particle states and also does not affect the Slater determinant $|\Phi_o\rangle$ preserving the distinction between occupied and virtual single–particle states. From the definitions of the matrices (10, 13) it can be seen that such a transformation of the single–particle basis also results in a unitary transformation of the secular matrix in (14) which preserves its block structure (16). Therefore also the FOSEP eigenvalue problem (19, 20) transforms without changing its eigenvalues. This argumentation can be transferred analogously to the closely related RPA and TDA. Summarising, we have seen that the FOSEP approximation as well as the RPA and TDA are invariant under unitary transformations within the set of virtual single–particle states. It is easily seen that this property generalises to unitary transformations of the orbital basis that do not mix occupied and virtual orbitals.

In a much more general sense, however, the matrix $\underline{\mathcal{H}}_{aa}$ of Eq. (5) which forms the primary block of the matrix representation $\underline{\mathcal{H}}$ of the excitation energy operator $\hat{\mathcal{H}}$ is invariant under (unrestricted) unitary transformations of the single particle space. Since the only unknown quantity in $\underline{\mathcal{H}}_{aa}$ (see also Eq. (A1) in the appendix) is the exact ground state of the system, the invariance properties of an approximation to $\underline{\mathcal{H}}_{aa}$ follow the chosen approximation for the ground state. In other words: The eigenvalues of the matrix of Eq. (A1) depend *only* on the chosen approximation for the ground state and *not* on the particular choice of the single–particle basis. In the special case of a system of particles which interact only with a one–particle potential, the primary block $\underline{\mathcal{H}}_{aa}$ is even independent of the ground state. In this case the first order already provides the exact solution for the excitation energies and is invariant with respect to any unitary transformations of the single–particle basis. This property is explained in more detail in Ref. [14].

D. Perturbation Theoretical Analysis of the Excitation Energies

In order to analyse the differences between the FOSEP approximation, the RPA, and the TDA we will now perform a perturbation theoretical analysis of the excitation energies up to second order and compare with straightforward Rayleigh–Schrödinger perturbation theory following Ref. [2]. Usually the Rayleigh–Schrödinger series itself is not a reliable method for calculating energies of excited states but it is very helpful for analysing and comparing different approximation schemes.

We assume that the Rayleigh–Schrödinger series starting from the singly excited Slater determinant

$$|\Phi_{\alpha\beta}\rangle = a_\alpha^\dagger a_\beta |\Phi_o\rangle \tag{27}$$

converges towards the excited state $|\Psi_{\alpha\beta}\rangle$. Note that here α has to be a particle index and β a hole index.

An expression for the second order excitation energy can be gained by subtracting the expressions for the ground state energy E_0 from the excited state energy $E_{\alpha\beta}$. Up to second order the ground state energy is given by the familiar expression

$$E_0(2) = E_0(1) + U_0^{(2p-2h)}, \tag{28}$$

where $E_0(1) = \langle\Phi_o| \hat{H} |\Phi_o\rangle$ is the first order ground state energy. The term

$$U_0^{(2p-2h)} = -\sum_{\substack{i<j \\ k<l}} \frac{\left|V_{ij[kl]}\right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_k - \varepsilon_l} \overline{n}_i \overline{n}_j n_k n_l \tag{29}$$

denotes the second order contribution to the ground state correlation. The given approximation is known as the Møller–Plesset (MP)–2 approximation and extensively used in quantum chemistry. In the Configuration Interaction language the second order term $U_0^{(2p-2h)}$ may be interpreted to present interactions of the ground state Slater determinant $|\Phi_o\rangle$ with two particle–two hole configurations.

The second order energy of the excited state is also evaluated straightforwardly and can be found in Ref. [2]. The excitation energy up to second order then reads

$$\Delta E_{\alpha\beta}(2) = E_{\alpha\beta}(2) - E_0(2)$$
$$= \Delta E_{\alpha\beta}(1) + U_{\alpha\beta}^{(p-h)} + U_{\alpha\beta}^{(2p-2h)} + R_{\alpha\beta} \tag{30}$$

where $\Delta E_{\alpha\beta}(1) = \varepsilon_\alpha - \varepsilon_\beta - V_{\alpha\beta[\alpha\beta]}$ is the first order excitation energy. The terms $U_{\alpha\beta}^{(p-h)}$ and $U_{\alpha\beta}^{(2p-2h)}$ denote second order contributions to the excited state's energy arising from the interaction of the configuration $|\Phi_{\alpha\beta}\rangle$ with (other) $p - h$ and $2p - 2h$ configurations, respectively, and can be found in Ref. [2]. The part $R_{\alpha\beta}$ is the remainder of a partial cancellation of the second order ground state correlation term $U_0^{(2p-2h)}$ of Eq. (29) with a contribution to the correlation of the excited state. It can be written as the sum of three terms

$$R_{\alpha\beta} = R_{\alpha\beta}^1 + R_{\alpha\beta}^2 + R_{\alpha\beta}^3 \tag{31}$$

where

$$R_{\alpha\beta}^1 = \sum_{\substack{j,k,l \\ k<l \\ k,l\neq\beta}} \frac{\left|V_{\alpha j[kl]}\right|^2}{\varepsilon_\alpha + \varepsilon_j - \varepsilon_k - \varepsilon_l} \overline{n}_j n_k n_l$$

$$R_{\alpha\beta}^2 = \sum_{\substack{i,j,l \\ i<j \\ i,j\neq\alpha}} \frac{\left|V_{ij[\beta l]}\right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_\beta - \varepsilon_l} \overline{n}_i \overline{n}_j n_l \tag{32}$$

$$R_{\alpha\beta}^3 = \sum_{j,l} \frac{\left|V_{\alpha j[\beta l]}\right|^2}{\varepsilon_\alpha + \varepsilon_j - \varepsilon_\beta - \varepsilon_l} \overline{n}_j n_l$$

These contributions are left over from $U_0^{(2p-2h)}$ corresponding to the special cases where $i = \alpha$ or $k = \beta$ in the sum of Eq. (29). The rest of $U_0^{(2p-2h)}$ is cancelled by contributions from the excited state.

We are now in the position to compare with the second order excitation energies from the TDA, the RPA, and the FOSEP scheme. The approximations for the excitation energies in these schemes are found by solving the eigenvalue problem related to the corresponding matrix. Basic matrix perturbation expansion leads to the second order approximation for the eigenvalue. We find the following:

$$\Delta E_{\alpha\beta}^{TDA}(2) = \Delta E_{\alpha\beta}(1) + U_{\alpha\beta}^{(p-h)} \tag{33}$$

$$\Delta E_{\alpha\beta}^{RPA}(2) = \Delta E_{\alpha\beta}(1) + U_{\alpha\beta}^{(p-h)} - R_{\alpha\beta}^3 \tag{34}$$

$$\Delta E_{\alpha\beta}^{FOSEP}(2) = \Delta E_{\alpha\beta}(1) + U_{\alpha\beta}^{(p-h)} + R_{\alpha\beta}^3 \tag{35}$$

All three approximation schemes are consistent in first order with the Rayleigh–Schrödinger expression (30). Therefore they are correctly referred to as first order schemes. The zeroth and first order contribution $\Delta E_{\alpha\beta}(1)$ originate in the diagonal matrix elements of the ph–ph block (TDA block) of the matrices $\underline{M}^{FOSEP}$ and $\underline{M}^{RPA}$ of Eqs. (19, 25) whereas the second order terms come in by the diagonalisation procedure. Neither of the three schemes reproduce the second order expression (30) completely. This is only achieved by more accurate and more costly schemes like ADC(2) or SOPPA.

The term $U_{\alpha\beta}^{(p-h)}$ describes part of the second order correlation of the excited state as can be seen from Eqs. (30) and (28, 29). It is the only second order contribution to the TDA excitation energy and originates in the off–diagonal part of the TDA matrix which also constitutes the ph–ph block of the FOSEP matrix $\underline{M}^{FOSEP}$. In the FOSEP and the RPA expressions the additional term $R_{\alpha\beta}^3$ is present which has already been identified as part of the ground state correlation. Comparing with the second order perturbation expansion (30), however, we notice that it appears with the wrong sign in the RPA excitation energy in contrast to FOSEP where the sign is consistent with the Rayleigh–Schrödinger expansion. This term comes in through the coupling of the ph with the hp block in the FOSEP matrix

$\underline{M}^{FOSEP}$ of Eq. (19) and the RPA matrix $\underline{M}^{RPA}$ of Eq. (25), respectively. We recall that the only difference between the FOSEP and the RPA equations are minus signs in the hp–hp blocks of the secular matrices and the RPA metric. These carry through to the second order expressions and prove inconsistent with Rayleigh–Schrödinger perturbation theory in the RPA case.

It is interesting to note that each of the three parts of $R_{\alpha\beta}$ of Eq. (32) is positive. Thus the RPA always lowers the TDA excitation energies in second order whereas the FOSEP approximation increases the energies in accordance with the positive sign of the full correction $R_{\alpha\beta}$. Taking into account that the TDA approximates the ground state by the variational Hartree–Fock method, it is sensible to expect an increase in the excitation energies when ground state correlation is additionally taken into account. Therefore we may conclude that the FOSEP scheme includes ground state correlation in a consistent way in contrast to the RPA which does not.

Concerning the term $U_{\alpha\beta}^{(2p-2h)}$ in the full second order expression (30) which is missing in all three schemes, we remark that it does not carry a definite sign (as can be seen from Eq. (68c) of Ref. [2]). It may, however, lower the energy of the excited state and thus can possibly overcompensate for the influence of the ground state correlation. In this way the RPA result may be supported by accidental numerical compensation.

E. Perturbation Theoretical Analysis of the Transition Moments

We now will show that transition operator matrix elements between the ground state and an excited state can, in contrast to TDA, be approximated by FOSEP consistently in first order. We consider the transition moment

$$\mathcal{T}_{\alpha\beta} = \langle \Psi_o | \hat{T} | \Psi_{\alpha\beta} \rangle \tag{36}$$

of the (one–particle) transition operator $\hat{T}$ for the particle–hole excited state $|\Psi_{\alpha\beta}\rangle$ that was introduced in the last paragraph. Up to first order the perturbation expansion yields

$$\mathcal{T}_{\alpha\beta}(1) = \langle \Phi_o | \hat{T} | \Phi_{\alpha\beta} \rangle + \langle \Phi_o | \hat{T} | \Psi_{\alpha\beta}^{(1)} \rangle + \langle \Psi_o^{(1)} | \hat{T} | \Phi_{\alpha\beta} \rangle. \tag{37}$$

Explicit expressions for these terms derive from straightforward Rayleigh–Schrödinger perturbation theory and may be found in Ref. [2].

In an analogous fashion to the preceding paragraph the above expression may be compared to the result of matrix perturbation analysis of the TDA, RPA, and FOSEP approximations for the transition moments. It is easily seen that the FOSEP eigenvalue problem (14, 19) together with the approximation for the transition moments of Eq. (15) leads to a consistent first order approximation of the transition moments. For the TDA, the RPA, and the first and second order ADC scheme the perturbation analysis has been carried out in Ref. [2]. It has been found that the TDA expression is incomplete in first order because the term $\langle \Psi_o^{(1)} | \hat{T} | \Phi_{\alpha\beta} \rangle$ is missing. This term is a consequence of first order ground state correlation which is neglected in the TDA. It is described correctly in the RPA which yields consistent transition moments through first order. This may be seen to justify the common statement that the RPA, in contrast to the TDA, considers ground state correlation. We want to mention that the transition moments are also described consistently through first order in the ADC(1), an approximation that is equivalent to the TDA with respect to the excitation energies but differs for the transition moments [2].

F. The Equivalence of Length and Velocity Form of the Dipole Operator Transition Moments

Now we will focus on the transition moments of the dipole operator as a particular choice for the transition operator. These transition moments are related to the so-called oscillator strengths and present important parameters characterising the interaction of the many–body system with radiation. There is a hierarchy of equivalent representations of the exact dipole operator transition moments, starting with the so–called length and velocity form. Without loss of generality we consider only the z–component $\hat{Z}$ of the dipole operator. The identity

$$(E_\mu - E_0)\langle \Psi_\mu | \hat{Z} | \Psi_o \rangle = -i \langle \Psi_\mu | \hat{P}_z | \Psi_o \rangle \tag{38}$$

expresses the equivalence between the length and the velocity form of the dipole operator transition moments defined by the left and the right hand side of this equation, respectively. The z–component of the momentum operator $\hat{P}_z$ is related to the dipole operator by $\left[\hat{H} , \hat{Z} \right] = -i\hat{P}_z$ provided that the Hamiltonian contains only local potentials like e. g.

for Coulomb interacting electrons in atoms or molecules. Eq. (38) then follows from the identity $(E_\mu - E_0)\langle\Psi_\mu| \hat{Z} |\Psi_o\rangle = \langle\Psi_\mu| \left[\hat{H} , \hat{Z} \right] |\Psi_o\rangle$.

It is a very special property of the RPA to preserve this equivalence exactly, provided the underlying Hartree–Fock single–particle basis is complete [27]. In fact the RPA eigenvalue problem may be derived setting out from a CI representation of the ground and excited state wavefunction and requiring certain 'hypervirial relations' which present a slight generalisation of the above mentioned equivalences [11]. Thus the exact fulfilment of these hypervirial relations may be regarded unique to the RPA while other approximation schemes show, at most, a perturbative equivalence. In order to make the perturbation expansion transparent, it is useful to introduce the function $\Delta(\lambda)$ as the difference between the right and the left hand side of Eq. (38). It is a function of the usual interaction strength parameter λ in $\hat{H}_\lambda = \hat{H}_0 + \lambda\hat{H}_1$. Owing to its non–local character, Hartree–Fock does not preserve the length–velocity equivalence. Hence, choosing $\hat{H}_0$ to be the Hartree–Fock operator, $\Delta(\lambda)$ does not vanish for any λ except for $\lambda = 1$. The expansion of $\Delta(\lambda)$ in powers of λ does not vanish term by term; each order will in general give a nonvanishing contribution. The TDA approximates only the zeroth order term of $\Delta(\lambda)$ correctly, giving an error in first order [i. e. $\mathcal{O}(\lambda)$]. The FOSEP approximates $\Delta(\lambda)$ through first order giving a second order error. So does the RPA which additionally has the unique property of reproducing the zero $\Delta(\lambda = 1) = 0$. For completeness we mention that the first order ADC [28] approximates $\Delta(\lambda)$ through first order while the SOPPA [29] as well as the second order ADC [28] are consistent through second order.

The result of equivalence through first order is another clue for the consistency of the FOSEP approximation. The error between length and velocity form provides a genuine test for the validity of the approximation. Depending on the particular aims of an approximate calculation this may seem more favourable than having an 'a priori' equivalence like in the RPA which hides the actual error with respect to the exact value of the transition moments.

III. APPLICATION TO A SIMPLE MODEL

In this section we compare the FOSEP approximation with the RPA, the TDA, and the exact solution for the excitation energies of a very simple model system. This model is commonly referred to as the Hubbard model for the Hydrogen Molecule H_2 [30]. In the model, all excitation energies can be calculated by analytic expressions in dependence of two parameters which mimic the effects of Coulomb interaction.

A. Definition of the Model and Exact Solution

The Hubbard model for the diatomic Hydrogen molecule represents each atomic site ($\mathbf{R}$ and $\mathbf{R'}$) by a single orbital electronic level denoted by $|\mathbf{R}\rangle$ and $|\mathbf{R'}\rangle$, respectively. Each level can be occupied by up to two electrons with opposite spin. The single–particle part of the Hamiltonian $\hat{h}$ contains a diagonal term

$$\langle\mathbf{R}| \hat{h} |\mathbf{R}\rangle = \langle\mathbf{R'}| \hat{h} |\mathbf{R'}\rangle = \mathcal{E} \tag{39}$$

which yields an energy $\mathcal{E}$ for each electron. The off–diagonal term describes attraction by the neighbouring nucleus and represents an amplitude for 'tunnelling' or 'hopping' of an electron from one site to another:

$$\langle\mathbf{R}| \hat{h} |\mathbf{R'}\rangle = \langle\mathbf{R'}| \hat{h} |\mathbf{R}\rangle = -t \quad (< 0) \tag{40}$$

Additionally a two–particle interaction term is present which yields a positive energy U whenever one level is occupied by two electrons. This term represents the intra–atomic Coulomb repulsion between two localised electrons. Note that all interactions are independent of electron spin.

We consider the neutral H_2 molecule, i. e. an occupation with two electrons. The solution of the Hartree–Fock equations yields the (molecular) orbital functions

$$|g\rangle = \frac{1}{\sqrt{2}}(|\mathbf{R}\rangle + |\mathbf{R'}\rangle) \qquad |u\rangle = \frac{1}{\sqrt{2}}(|\mathbf{R}\rangle - |\mathbf{R'}\rangle). \tag{41}$$

while the corresponding Hartree–Fock single–particle energies read $\varepsilon_{g/u} = \mathcal{E} \mp t + \frac{1}{2}U$. In the Hartree–Fock ground state Slater determinant $|\Phi_o\rangle = |g \uparrow g \downarrow\rangle$ the orbital $|g\rangle$ is doubly occupied. In order to make transparent the transition between the Hartree–Fock approximation and the correlated problem we introduce the additional (perturbation) parameter $\lambda \in [0, 1]$ by using the Hamiltonian

$$\hat{H}_\lambda = \hat{H}_o + \lambda \hat{H}_1 \tag{42}$$

where the Fock operator $\hat{H}_o$ and the interaction Hamiltonian $\hat{H}_1$ are defined as in Sec. I. The matrix elements of the two–body interaction V_{ijkl} that define $\hat{H}_1$ are given by the transformation (41) into the atomic orbital picture.

There are six independent solutions for the two–electron eigenstates of the system. According to the possible combinations of the electrons' spins three states of singlet symmetry $|\Psi_{0/1}\rangle$ and $|S_u\rangle$ and a degenerate triplet $|T_{-1/0/1}\rangle$ are found. The triplet and the singlet $|S_u\rangle$ states are uncorrelated and have one electron in a u and one in a g orbital. The singlet state $|\Psi_1\rangle$ corresponds to a $2p - 2h$ excitation. It will no longer be considered because it lies outside of the range of RPA, TDA, and FOSEP. The wavefunction of the singlet ground state is given by

$$|\Psi_0\rangle_\lambda = \alpha_\lambda |g \uparrow g \downarrow\rangle + \beta_\lambda |u \uparrow u \downarrow\rangle \tag{43}$$

where

$$\begin{aligned}
\alpha_\lambda &= \frac{4\,t + \sqrt{16\,t^2 + \lambda^2\,U^2}}{\sqrt{\lambda^2\,U^2 + \left(4\,t + \sqrt{16\,t^2 + \lambda^2\,U^2}\right)^2}} \\
\beta_\lambda^2 &= 1 - \alpha_\lambda^2.
\end{aligned} \tag{44}$$

The dependence on the perturbation parameter λ indicates the influence of correlation which only appears between the singlet Slater determinants of g symmetry $|g \uparrow g \downarrow\rangle$ and $|u \uparrow u \downarrow\rangle$. In order to simplify the notation, we will drop the subscript λ in the following. Note that the uncorrelated case corresponds to $\lambda = 0$ where $\alpha = 1$ and $\beta = 0$. Therefore it is clear that $|\Psi_o\rangle$ is connected to the Hartree–Fock ground state $|\Phi_o\rangle = |g \uparrow g \downarrow\rangle$. The energy eigenvalues of the exact states are given by

$$\begin{aligned}
E_0 &= 2\,\mathcal{E} + U - \tfrac{\lambda}{2}\,U - \sqrt{4\,t^2 + \tfrac{\lambda^2}{4}\,U^2} \\
E_{S_u} &= 2\,\mathcal{E} + U \\
E_T &= 2\,\mathcal{E} + U - \lambda\,U
\end{aligned} \tag{45}$$

The excitation energies ΔE_i are defined as usual by the difference of the excited state's energy E_i to the ground state energy E_0. The energy related to the excitation into the triplet, e. g., is thus given by

$$\Delta E_T = E_T - E_0 = -\frac{\lambda}{2}\,U + \sqrt{4\,t^2 + \frac{\lambda^2}{4}\,U^2} \tag{46}$$

Note that the expansion of ΔE_i into a power series in λ yields the Rayleigh–Schrödinger series of the excitation energies which has been discussed in a general context in Sec. II D.

B. Results for TDA, RPA, and FOSEP

We now discuss approximations to the (singlet) excitation from $|\Psi_o\rangle$ into $|S_u\rangle$ and the (triplet) excitation into one of the $|T_i\rangle$ states. E. g. the triplet excitation into $|T_{-1}\rangle$ is defined by a particle–hole excitation from the $|g \downarrow\rangle$ to the $|u \uparrow\rangle$ orbital. The TDA matrix for this triplet excitation is one dimensional because the excited state is uncorrelated. Therefore the TDA result for the triplet excitation energy

$$\Delta E_T^{TDA} = 2t - \frac{\lambda}{2}U \tag{47}$$

coincides with the first order of Rayleigh–Schrödinger perturbation theory.

The FOSEP matrix $\underline{\underline{M}}^{FOSEP}$ as well as the RPA matrix, however, have dimension two because of the coupling with the corresponding hole–particle configuration. The FOSEP matrix for the triplet excitation is given by

$$\underline{\underline{M}}_T^{FOSEP} = \begin{pmatrix} 2t - \frac{\lambda}{2}U & \frac{\lambda}{2}U \\ \frac{\lambda}{2}U & -2t - \frac{\lambda}{2}U \end{pmatrix} \tag{48}$$

Its eigenvalues are given by

$$\Delta E_T^{FOSEP(p/u)} = -\frac{\lambda}{2}U \pm \sqrt{4\,t^2 + \frac{\lambda^2}{4}\,U^2} \tag{49}$$

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As discussed in Sec. I we obtain physical and unphysical eigenvalues of which the latter do not carry any physically relevant information. The distinction between the physical and the unphysical eigenvalue is clear in the present case because $\Delta E_T^{FOSEP(p)}$ is always non–negative while $\Delta E_T^{FOSEP(u)}$ is non–positive for all choices of the parameters. Note that the physical eigenvalue yields the exact excitation energy $\Delta E_T^{FOSEP(p)} = \Delta E_T$!

The close relation of the RPA eigenvalue problem to the FOSEP matrix was discussed in Sec. II A. The solutions of the RPA equations for the triplet excitation are given by

$$\Delta E_T^{RPA(p/u)} = \pm \sqrt{4\,t^2 - 2\,\lambda\,t\,U} \tag{50}$$

Obviously the expression under the square root may become negative for certain choices of the parameters, in which case the RPA becomes unstable.

A plot of the solutions of the FOSEP, the RPA, and the TDA equations as a function of the perturbation parameter λ for a particular choice of the Hubbard parameters t and U can be found on the top of Fig. 1. For this choice representing strong interatomic Coulomb repulsion, the RPA becomes instable. As discussed in Sec. II D in the framework of a second order analysis, the RPA lowers the TDA value whereas the FOSEP approximation yields a higher value for the excitation energy which is correct in the present case. We have already mentioned that here only the ground state $|\Psi_o\rangle$ is correlated whereas the excited state $|T_{-1}\rangle$ is not. This ground state correlation is correctly taken into account by the FOSEP approximation but not by the RPA. In the present simple model this goes even beyond second order as can be seen from Eq. (46).
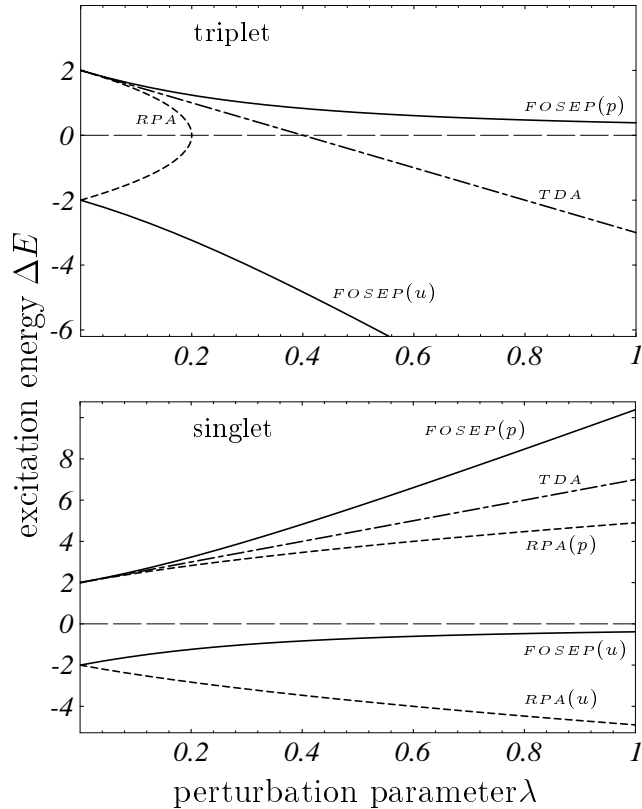

FIG. 1. The eigenvalues of the FOSEP, RPA, and TDA equations for the triplet and the singlet excitation as described in the text. The physical FOSEP excitation energies $\Delta E^{FOSEP(p)}$ (labelled as $FOSEP(p)$) coincide with the exact excitation energies. The parameters of the Hubbard model are chosen as $t = 1$ and $U = 10$. All energies are given in units of $\mathcal{E}$. For the triplet excitation, the RPA becomes instable yielding complex eigenvalues for $\lambda > 0.2$.

For the singlet excitation, results analogous to the triplet case are found. Again the FOSEP result $\Delta E_{S_u}^{FOSEP(p)}$ coincides with the exact excitation energy $\Delta E_{S_u} = E_{S_u} - E_0$. The TDA result evaluates to

$$\Delta E_{S_u}^{TDA} = 2t + \frac{\lambda}{2}U \tag{51}$$

while the RPA yields

$$\Delta E_{S_u}^{RPA(p)} = \sqrt{4\,t^2 + 2\,\lambda\,t\,U}. \tag{52}$$

A plot of these result with the same choice of parameters as for the triplet excitation is shown at the bottom of Fig. 1.

The Hubbard parameters used for the plots in Fig. 1 have been chosen such that the differences between the three first order approximations are large and become apparent. When the on–site repulsion term U is decreased in comparison to the hopping parameter t, the RPA becomes stable and the differences between the discussed approximations diminish. From Eq. (44) it can be seen that U is the source of ground state correlation in the model. Thus the present analysis supports the findings of Sec. II D and leads to the conclusion that among the three considered approximations for excitation energies only the FOSEP method includes ground state correlation in a consistent manner.

Of course, it is a special peculiarity of the present simple model that the FOSEP approximation already yields the exact excitation energies. Certainly this model may seem inadequate to draw conclusions on the performance of FOSEP for realistic large finite quantum systems which constitute the main area of possible applications. Therefore, this model should not be understood as a test for large–scale numerical calculations but rather as the simplest possible system where the effect of ground state correlation could be investigated analytically.

IV. CONCLUSIONS

In this paper we have presented a novel approximation scheme for the calculation of energies and transition moments of many–body systems. It derives from the first order approximation to the self energy of a recently proposed extended particle–hole Green's function [14]. The resulting approximations for excitation energies and transition moments prove consistent in first order but also higher order terms are present. Starting out from a Hartree–Fock single–particle description, the FOSEP approximation yields a matrix eigenvalue problem of the same size as the well known Random Phase Approximation (RPA). In contrast to the RPA, however, FOSEP presents a hermitian eigenvalue problem and thus avoids the instabilities of the RPA. Although the FOSEP approximation has many properties in common with the RPA, like size consistency and the invariance with respect to unitary transformations of the Hartree–Fock virtual orbitals, there are also substantial differences. We have shown by a perturbation theoretical analysis up to second order that the FOSEP approximation for the excitation energies consistently includes part of the ground state correlation whereas the RPA proves inconsistent in this respect. This statement is supported by the results of a very simple exactly solvable model. In the considered model the ground state is correlated whereas the approximated excited states are not. It turned out that the FOSEP approximation yields the exact results for the excitation energies whereas the RPA does worse than the simpler Tamm–Dancoff approximation (TDA). We also have addressed the equivalence of length and velocity form of the transition moments. The exact preservation of this equivalence is a very peculiar property of the RPA. Within the FOSEP approximation this equivalence is only preserved in first order which is consistent for a first order scheme. The second order error encountered, however, may provide useful in estimating the applicability of the approximation.

Future calculations on realistic systems still have to provide the ultimate test for the usefulness of the approximation scheme presented here. From the present point of investigation the FOSEP method seems to have excellent prospects to find widespread application like, e. g., in clarifying the electronic structure of larger molecules especially when ground state correlation is important. A possible line of extending the FOSEP method is to start out from a multi–configurational self consistent field (MC-SCF) reference state instead of the Hartree–Fock Slater determinant $|\Phi_o\rangle$. This would allow for an adequate treatment of open–shell or other systems where strong ground state correlation prohibits the zeroth order description by a Slater determinant. The first order particle–hole self energy seems ideally suited for such an extension since the primary matrices are defined without reference to occupied or virtual Hartree–Fock orbitals in contrast to the RPA or TDA. Thus the inclusion of multi–configurational reference states provides a natural extension of the present theory. Straightforward approximations to the static particle–hole self energy can also be obtained from a ground state description by density functional theory (DFT). While DFT has been very successful in predicting ground state properties, the DFT description of excited states is a vivid and still open field of current interest [31,32,33,13]. The static particle–hole self energy seems well suited for adaption to DFT since it provides a simple model for excitation properties that only requires a decent approximate description of one and two particle densities in the ground state as input as discussed in the appendix. A direct formulation of the particle–hole self energy in terms of density functionals, on the other hand, may as well lead to powerful approximations. Another open point is the development of higher order approximations to the particle–hole self energy. This will allow to increase the accuracy and lift the present restriction to particle–hole type excitations. A realisation of systematic higher order approximations could follow the concepts of correlated excited states and intermediate state representations developed in Refs. [18,19] and is left for future work.

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APPENDIX

The general formalism behind the theory of extended two–particle Green's functions is described thoroughly in Ref. [14] where also the definition of the states $|Y_{rs}\rangle$, the metric $\hat{\mu}$, and the generalised excitation energy operator $\hat{\mathcal{H}}$ can be found. Here we only want to show one result of the general theory: The general expression for the primary block $\underline{\underline{\mathcal{H}}}_{aa}$ of the excitation energy operator matrix is given by

$$
\begin{aligned}
\left[\underline{\underline{\mathcal{H}}}_{aa}\right]_{rs,r's'} &= \langle Y_{rs}|\hat{\mu}\hat{\mathcal{H}}|Y_{r's'}\rangle \\
&= \langle \Psi_o| \left[a_s^\dagger a_r,\, \left[\hat{H},\, a_{r'}^\dagger a_{s'}\right]\right] |\Psi_o\rangle \\
&\quad + \langle \Psi_o| \left\{\left[\hat{H},\, a_{r'}^\dagger\right],\, a_r\right\} |\Psi_o\rangle\langle\Psi_o| a_{s'}a_s^\dagger |\Psi_o\rangle \\
&\quad + \langle \Psi_o| \left\{a_r,\, a_{r'}^\dagger\right\} |\Psi_o\rangle\langle\Psi_o| \left[\hat{H},\, a_{s'}\right] a_s^\dagger |\Psi_o\rangle \\
&\quad + \langle \Psi_o| \left[\hat{H},\, a_{r'}^\dagger\right] a_r |\Psi_o\rangle\langle\Psi_o| \left\{a_{s'},\, a_s^\dagger\right\} |\Psi_o\rangle \\
&\quad + \langle \Psi_o| a_r a_{r'}^\dagger |\Psi_o\rangle\langle\Psi_o| \left\{\left[\hat{H},\, a_{s'}\right],\, a_s^\dagger\right\} |\Psi_o\rangle.
\end{aligned}
\tag{A1}
$$

Here $|\Psi_o\rangle$ denotes the exact ground state of the system. In general, Eq. (A1) requires the evaluation of ground state expectation values of one and two–particle operators. This is due to the particular combination of commutators and anticommutators and to the fact that the Hamiltonian $\hat{H}$ is a two–particle operator. But this means that the primary block $\underline{\underline{\mathcal{H}}}_{aa}$ and therefore the static particle–hole self energy can be calculated exactly if the general one and two–particle densities of the ground state are known. Approximating the exact ground state $|\Psi_o\rangle$ by a Slater determinant leads to a factorisation of the two–particle densities and the first order expression (12) is obtained. Other approximations for the densities than those obtained by the Hartree–Hock Slater determinant are of course also possible. Density functional theory, on the one hand, or a multi–configurational self consistent field (MC–SCF) approximation for the ground state wavefunction, on the other hand, provide interesting alternative approaches.

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